

NOVEL PHENYLETHYNYL IMIDE SILANES AS COUPLING AGENTS FOR TITANIUM ALLOY

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INTRODUCTION

The durability of titanium (Ti) alloys bonded with high temperature adhesives such as polyimides has failed to attain the level of performance required for many applications. The problem to a large part is attributed to the instability of the surface treatment on the Ti substrate. Although Ti alloy adhesive specimens with surface treatments such as chromic acid anodization, Pasa-Jell, Turco, etc. have provided high initial mechanical properties, these properties have decreased as a function of aging at ambient temperature and faster, when aged at elevated temperatures or in a hot-wet environment. As part of the High Speed Civil Transport program where Ti honeycomb sandwich structure must perform for 60,000 hours at 177°C, work was directed to the development of environmentally safe, durable Ti alloy surface treatments.

APPROACH

The work presented herein involved development of a sol-gel surface treatment using various phenylethynyl containing imide silanes and tetraethoxysilane (TEOS) to form an organic/inorganic hybrid surface on Ti alloy. A novel aromatic phenylethynyl imide silane (APEIS) and pendent phenylethynyl imide oligomeric disilane (PPEIDS) were prepared, and sol-gel solutions containing the new silanes and TEOS were formulated to develop a system that provided a gradient hybrid interphase between metal and polyimide adhesive. A two-step chemical process was initially employed for the surface pretreatment to produce an oxide layer [1]. Standard single lap specimens were fabricated using a phenylethynyl terminated imide oligomer as the adhesive and tensile shear tests were performed. Morphology of the interphase between the metal and the adhesive was investigated using scanning electron microscopy (SEM). Chemical composition of the interphase was analyzed by X-ray photoelectron spectroscopy (XPS) and SEM using an X-ray mapping mode and energy dispersive spectroscopy. Depth profile of the interphase was explored using Auger electron spectroscopy (AES). These analyses have allowed an assessment of how the bonding is affected by various sol gel solutions, concentrations, and environments. The new silanes were also investigated as coupling agents for an E-glass carrier used to produce a supported adhesive film.

EXPERIMENTAL

The general chemical structures of APEIS and PPEIDS are presented in Fig. 1. Various sol-gel solutions were prepared as shown in Fig. 2. The primary sol-gel solutions studied were PETI-5/APEIS/TEOS and PPEIDS/TEOS. Organic and inorganic precursors were mixed in N-methyl-2-pyrrolidinone (NMP) to form a transparent solution. Distilled water was added to hydrolyze the alkoxy silane groups. The solution was filtered and the filtrate was stirred at least 12 hr at RT before applying onto a metal substrate. Ti alloy (Ti, 6Al-4V) specimens pretreated by a two-step chemical process using sulfuric acid and

alkaline perborate were dipped into the prepared solution for 3 min. The sol-gel treated panels were dried in an oven at 110 and 220°C for 30 min each, and then allowed to cool slowly to RT in the oven.

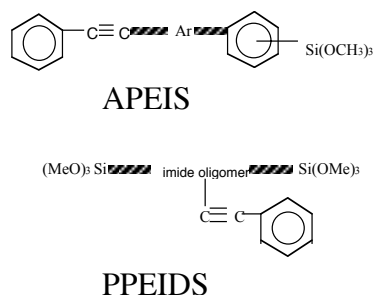


Figure 1. Schematic of the chemical structures of aromatic imide silanes (NASA/LaRC).

Sol-gel solutions: Organic/inorganic/NMP/H₂O
 Organic: PETI-5, PPEIDS, or APEIS, 85PETI-5/15APEIS
 Inorganic: TEOS
 Organic:inorganic = 85:15
 Organic: NMP = 15:85
 TEOS:H₂O = 1:1

Figure 2. Compositions of sol-gel solutions.

Single lap shear specimens were bonded using an adhesive tape (FM-X5, Cytec) in either a hydraulic press or an autoclave at 371°C under 50 psi for one hour. The strengths of the lap shear specimens were tested at RT, 177°C, RT after a 3 day water-boil, and RT after aging at 177°C according to ASTM D1002. An SEM (JSM-6400) was employed to analyze the surface morphology and chemical composition using PGT (Princeton Gamma-Tech) Prism Digital Spectrometer for EDX and X-ray mapping. The samples for SEM were prepared by polished sections of the Ti alloy treated with various sol-gel solutions after embedding the metal into an epoxy mold. The chemical composition of the surface of the specimen was analyzed by XPS (5400-XPS) and the depth profiling was performed using AES (610 scanning Auger system). The solutions were cast onto a glass plate to prepare thin films for Thermogravimetric analysis (TGA).

RESULTS AND DISCUSSION

Sol-gel solution

Fig. 3 shows the effects of the various solutions on the lap shear strengths. 15% PETI-5 solution exhibited excellent RT strength but only 60% retention of the RT strength after a 3-day water-boil. 15% PETI-5/TEOS sol-gel solution exhibited very poor performance at both RT and at RT after a 3- day water-boil, probably due to a lack of chemical bonding between the organic and inorganic phases. 15% PETI-5/APEIS/TEOS solution showed almost equivalent RT strength as PETI-5 and 93% retention of the RT strength after a 3-day water-boil. Since APEIS has a phenylethynyl group on one end of the molecule and three alkoxy groups attached to silicon at the other end of the molecule, PETI-5 and TEOS are most likely chemically bonded to produce a homogeneous hybrid structure at the interface, providing excellent performance after a 3-day water-boil. TGA analysis of the transparent film of 15% PETI-5/APEIS/TEOS showed 5% weight loss at 475°C.

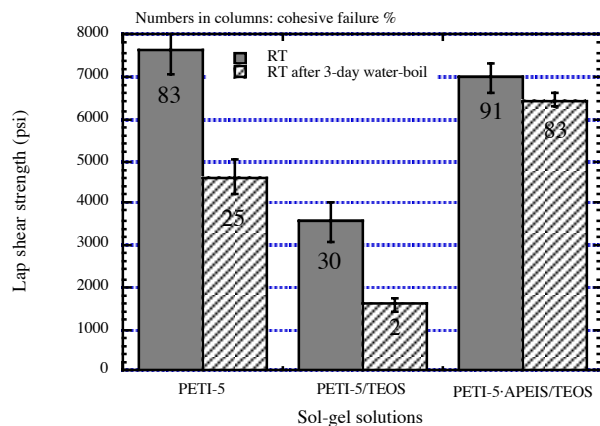


Figure 3. Lap shear strengths: sol-gel solution effect.

PPEIDS was also employed to replace the PETI-5-APEIS mixture since PPEIDS has a PETI-5 backbone with a pendent phenylethynyl group and trialkoxy silane groups at both ends of the molecule. RT strength of 8800 psi with 95% cohesive failure and RT strength of 8108 psi with 91 % cohesive failure after a 3-day water-boil were attained with the 15% PPEIDS/TEOS solution (Fig. 4).

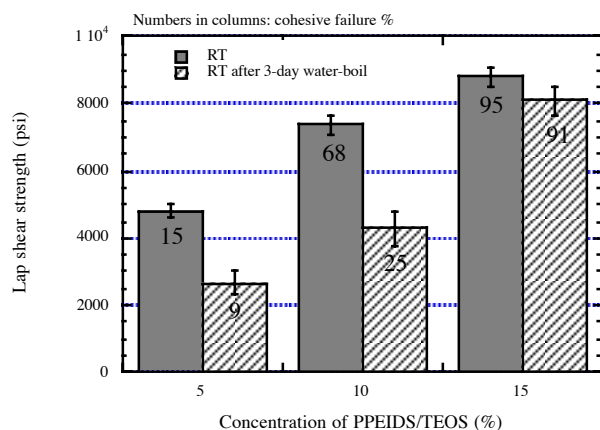


Figure 4. Lap shear strengths: concentration effect.

Concentration

Fig. 4 shows the lap shear strength data for PPEIDS/TEOS specimens with strengths at RT and RT after a 3-day water boil increasing with the concentration of the solution (i.e. sol-gel layer thickness). Significant improvement in tensile shear strengths was found at RT after a 3-day water boil. This increase presumably arises from a thicker coating layer, providing a priming effect since no primer was applied for the adhesive bonding. The same trend was observed with the data from the PETI 5/APEIS/TEOS specimens.

Morphology

PETI-5-APEIS/TEOS and PPEIDS/TEOS solutions usually formed slightly thicker layers (1.5-2.0 μm) than APEIS/TEOS ($\approx 1.0 \mu\text{m}$) according to the SEM and AES depth

profiling. While the former two usually form transparent film, representing homogeneous organic inorganic hybrid, the latter afforded an opaque film with much lower thermal stability according to the TGA results. Furthermore, PPEIDS/TEOS and PETI-5/APEIS/TEOS solutions usually exhibited better wetting on the Ti alloy than the APEIS/TEOS solution. The surface of the pretreated metal was rougher than the surface of the sol-gel layer because the imide containing solutions have good planarizability, resulting in uniform bonding with the adhesive tape (Fig. 5(a)).

Chemical composition

X-ray mapping, EDX and XPS were employed to identify the chemical composition of the interfacial zone. Figures 5 and 6 are examples of the X-ray maps and EDX line mapping of the polished sections of the metal treated with 15% PETI-5/APEIS/TEOS, respectively. The sol-gel layer appeared ca. $2\mu\text{M}$ thick in Fig. 5(a) and the Si peak (hatched area) in Fig. 6. The X-ray maps revealed that relatively more Si appeared close to the metal while more organic appeared toward the sol gel surface. This was more obvious in the Si and C peaks in the EDX map. XPS data also shows preferential Si diffusion toward the metal substrate during the high temperature bonding process (371°C), which further supports the formation of a Si gradient sol-gel layer. The same behavior was observed for PPEIDS/TEOS sol-gel layer specimen.

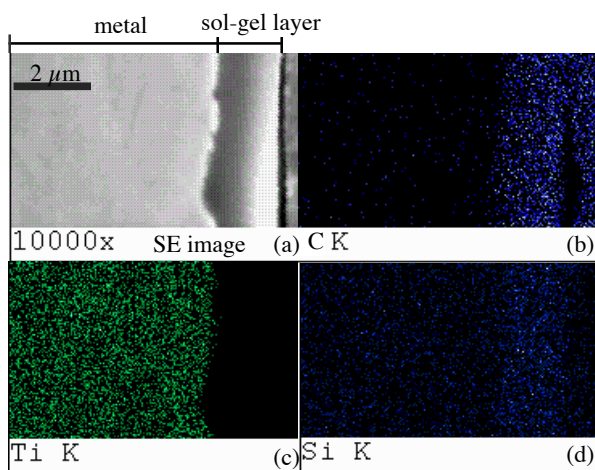


Figure 5. X-ray maps of 15% PETI-5·APEIS/TEOS.

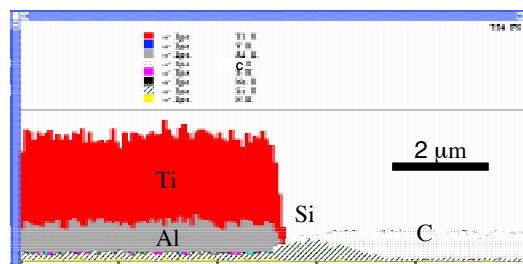


Figure 6. EDX line map of 15% PETI-5·APEIS/TEOS.

Coupling agent application for scrim fabric

Either APEIS or PPEIDS was applied to a 112 E-glass scrim fabric as a coupling agent and then followed by a PETI-5 coating to produce an adhesive tape. Lap shear specimens were prepared using the 15% sol-gel solution and were tested. The failure surfaces

exposed 100% cohesive failure though the value was somewhat low (5699 psi, Fig 7). This is possibly due to the unoptimized processing condition (371 °C for one hour at 50 psi).



Figure 7. Lap shear failure surface: 15% PETI-5·APEIS/TEOS solution with 112 E-glass scrim cloth treated with APEIS and PETI-5 coating (5699 ± 157 psi).

SUMMARIZING REMARKS

Novel sol-gel solutions from new phenylethynyl imide silanes were applied to Ti-6-4 alloy to develop a surface for hot-wet environments. Silane concentration can be controlled by altering the molecular weight of the imide oligomer. The PPEIDS/TEOS sol-gel layer exhibited RT strength of 8800 psi with 95% cohesive failure and RT strength after a 3-day water-boil of 8108 with 91 % cohesive failure. SEM and AES depth profile revealed 1-2 μm thick sol-gel layer having higher Si concentration near the metal substrate, which may have contributed to the high strength and durability in the hot wet environment. XPS and TGA data support that PETI-5/APEIS/TEOS or PPEIDS/TEOS solution forms a stable homogeneous hybrid structure at the interface to provide robust bonding. This provides a substitute for the conventional primer. These new sol-gel formulations can potentially be applied to any metal adherend for bonding with any phenylethynyl containing imide adhesive to provide stability for hot-wet environments without using chromium compounds and mechanical abrasion in the surface preparation.

REFERENCES

1. C. Park et al, NASA/LaRC, private comm.

ACKNOWLEDGEMENTS

We thank Professor John G. Dillard for his help in experiments for the XPS and AES depth profile data.